

ABSTRACT

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(I) THE EFFECT OF SOLVENT AND SHIFT REAGENTS ON THE PROTON MAGNETIC RESONANCE SPECTRA OF SOME CUBANE DERIVATIVES

(II) ON THE MECHANISM OF PHOTODIMERIZATION OF CYCLOPENTADIENE

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Thesis dated December 1976

Part I of this thesis is concerned with the effect of solvent, substituents and the shift reagent $\text{Eu}(\text{DPM})_3$ on the proton magnetic resonance spectrum of several 1,4-disubstituted cubane derivatives. The chemical shift of the cubane protons is insensitive to aliphatic solvents, but there is an upfield shift of the cubane protons in benzene- d_6 relative to the position in carbon tetrachloride. Electron-withdrawing substituents and the shift reagent induce a downfield shift for the cubane proton resonances.

Part II describes a reinvestigation of the photochemistry of cyclopentadiene in an attempt to offer an explanation of the product distribution in the sensitized irradiation. Unfortunately, sensitized and unsensitized irradiations carried out at -60° and 0° , with low and high pressure ultraviolet light sources, were too inconclusive to permit meaningful conclusions to be drawn.

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RESONANCE SPECTRA OF SOME CUBANE DERIVATIVES

(II) ON THE MECHANISM OF PHOTODIMERIZATION OF CYCLOPENTADIENE

A THESIS

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FOREWORD

This thesis is divided into two unrelated parts. Part I is concerned with the effect of solvent and shift reagents on the proton magnetic resonance spectra of some cubane derivatives. Part II summarizes some unsuccessful attempts at studying the mechanistic details of the photodimerization of cyclopentadiene. The experimental work was completed in September, 1972.

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PART I

The Effect of Solvent and Shift Reagents on the
Proton Magnetic Resonance Spectra of Some Cubane Derivatives

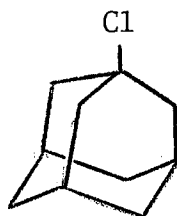
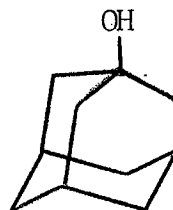
INTRODUCTION

Significant differences are observed in chemical shifts measured from internal references when solvent, concentration or temperature are altered. It follows from this that the chemical shifts for proton resonances in many compounds are a function of the solvent used. In fact, variation of solvent is a technique often used to simplify spectra by removing the effects of accidental or near equivalence.¹ Deuterium exchange is one of the earlier known techniques used in the simplification of nuclear magnetic resonance (nmr) spectra. Generally, protons attached to oxygen, nitrogen, and sulfur will exchange with deuterons in deuterium oxide. The compound is dissolved in a water-immisible solvent. A few drops of deuterium oxide are added, followed by vigorous shaking and finally centrifuging. A rapid equilibrium takes place between active hydrogens in the molecule and the deuteriums. Thus, the relative number of exchangeable protons can be determined by the HDO absorption near 6.1,2

The most dramatic solvent effect is that associated with aromatic solvents. The shifts observed with benzene (vs. CCl₄ or CDCl₃) as solvent have been attributed to intermolecular interactions and appear to reflect the diamagnetic anisotropy of aromatic compounds and their ease of complex formation. Because these complexes do form, information about the stereochemistry of a molecule can be obtained by studying solvent shifts.¹ Ronayne and Williams³ suggest that the observed solvent shifts induced by benzene are due to a 1:1 interaction between solute and solvent. On the other hand, the evidence of Fort and

Lindstrom⁴ suggests that in the case of solvent-induced chemical shifts, the observed effect is not due to a 1:1 type interaction but is instead due to a slight structuring of the solvent about each solute molecule.

Fort and Schleyer⁵ have studied solvent and substituent effects on several adamantane derivatives. Interestingly, the beta protons closest to the substituent are affected least by a change in solvent. In addition, since the molecule is fairly rigid, substituents cannot affect the bond angle. Therefore the change in chemical shift with different substituents is in fact due to the substituents. Because many resonance lines do overlap, much structural information is lost. However, with adamantane derivatives, a change of solvent can often induce selective shifts in parts of the molecule, thus permitting details obscured under normal conditions to be revealed. For example, 1-chloroadamantane, 1, in carbon tetrachloride gives two broad singlets: one at 1.1 ppm due to the beta and gamma protons and the other at 1.7 from the delta protons. In benzene all the protons are separated: beta at 2.0, gamma at 1.75, and delta at 1.35 ppm. A similar effect is seen in 1-hydroxyadamantane, 2. The beta and delta resonances overlap in carbon tetrachloride at 1.6 ppm and the gamma and the hydroxyl appear at 2.1 and 1.3 ppm, respectively. However, in benzene, the signals appear at 1.6, 1.9, 1.4, and 1.1 for the beta, gamma, delta and hydroxyl protons, respectively. This type of selective separation of peaks by solvents has also been reported for the disubstituted adamantanes.⁵

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The chemical shift of the beta methylene protons of 1-aminoadamantane and 1-adamantanecarboxylic acid are 1.55 and 1.94, respectively, compared to 1.78 in the unsubstituted adamantane. This shows a pronounced substituent effect for both electron-withdrawing and electron-donating groups. However, the chemical shift of the bridgehead protons, two carbons removed, shows no substituent effect; i.e., 2.04 and 2.03 for the amine and carboxylic acid, respectively.

In addition to chemical shifts induced by solvents, substantial differences have been observed with shift reagents. Nuclear magnetic resonance reagents are paramagnetic lanthanide complexes that complex with compounds having lone electron pairs.

The first use of lanthanide complexes as shift reagents was reported by Hinckley.⁶ He observed that the addition of the dipyridine adduct of tris(dipivalomethanato)europium ($\text{Eu}(\text{DPM})_3 \cdot 2\text{py}$) to cholesterol resulted in substantial shifts of the cholesterol peaks to lower field. In addition there was very little line broadening. Because pyridine competes with the shift reagent for association with the substrate, Sanders and Williams⁷ reasoned that the pyridine free complex,

tris(dipivalomethanato)europium III ($\text{Eu}(\text{DPM})_3$), should produce even more substantial shifts. Indeed this was the case; they reported that the shifts observed with the pyridine free adduct and cholesterol were increased by a factor of four over those with $\text{Eu}(\text{DPM})_3 \cdot 2\text{py}$ at comparable concentrations. Sanders and Williams also compared the spectra of other alcohols with $\text{Eu}(\text{DPM})_3$.

For n-hexanol, the following observations were made at 100 MHz in carbon tetrachloride with and without the addition of 0.29 molar equivalents of $\text{Eu}(\text{DPM})_3$:

	HO	-	CH ₂	-	CH ₂	-	CH ₂	-	CH ₂	-	CH ₂	-	CH ₃
without $\text{Eu}(\text{DPM})_3$	2.75 broad singlet		3.5 broad singlet				1.2-1.7 multiplet						0.90 trip.
with $\text{Eu}(\text{DPM})_3$	*		10 trip.		5.5 quin.		4.2 quin.		2.7 quin.		2.2 sex.		1.4 trip.

* The signal of the hydroxyl proton is shifted too far to be recorded.

The signal from the t-butyl group of $\text{Eu}(\text{DPM})_3$ appears at higher field than tetramethylsilane and does not interfere with the spectra since most induced shifts are to lower field. The largest shift changes occur for those protons closest to the coordination site. Further, the amount of the shift falls off with distance. Therefore shift reagents are especially useful when interpreting spectra of compounds having similar chemical shifts. In many cases the addition of $\text{Eu}(\text{DPM})_3$ to samples yields first order spectra.

Sanders and Williams⁷ also reported that europium complexes with

functional groups having lone pairs. Amines and alcohols complex strongest, ketones complex 35-40% less strongly than alcohols, and ethers and esters even less. This applies for molecules in which the amount of steric hindrance is small. The complex decomposes slowly in the presence of phenolic and carboxylic acid groups. Demarco and co-workers⁸ have shown that up to equimolar amounts, the amount of shift induced by a shift reagent is concentration-dependent.

Wahl and Peterson⁹ have suggested that the mechanism of deshielding involves interactions through space and through bonds. The shifts appear to originate from a secondary magnetic field generated by the magnetic moment of the paramagnetic ion. Though pseudocontact in nature, the shifts are predictable with the exception of the protons on the carbon bonded to the coordinating atom. These shifts appear to be produced by contact with the shift reagent. The reagent presumably exhibits its effect by establishing a rapid (on the nmr time scale) equilibrium between a labile complex of $\text{Eu}(\text{DPM})_3$ with a Lewis base and unassociated solutes. The effect of the shift reagent on the substrate appears to be both distance- and angle-dependent. This has been used to indicate relative distances from coordination groups and has allowed assignment of resonance lines on this basis. In addition, information about stereochemistry has been obtained from the use of shift reagents.

That the shifts do indeed result from interactions through space was shown in the nmr study of adamantane-1-ol (2) by Wahl and Peterson.⁹

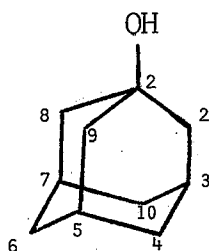
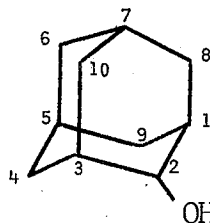
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Table 1. The Effect of $\text{Eu}(\text{DPM})_3$ on the NMR Spectrum of Adamantane-1-ol at a 0.4:0.6 Mole Ratio of $\text{Eu}(\text{DPM})_3$ and 2 in CDCl_3 .*

Hydrogens	$d_{\text{Eu-H}}(\text{\AA})$	Number of Intervening Bonds (Eu-H)	$\Delta\omega(\text{Hz})$
2,8,9 (6H)	2.77	4	268
4,6,10- <u>cis</u> (3H)	4.82	6	87
3,5,7 (3H)	5.03	5	81
4,6,10- <u>trans</u> (3H)	6.34	6	66

* Taken from G. H. Wahl, Jr. and M. R. Peterson, Chem. Comm., 1167 (1970).

If the mechanism of shift reagents were strictly via bonds, the chemical shift of the 3, 5, and 7 protons would be greater than the cis-4, 6, and 10 protons. However, this is not the case. Further evidence for the importance of the interactions through space was shown with adamantane-2-ol (3). The 8-, 10-cis and trans hydrogens and 4-, 9-cis and trans hydrogens are both separated from the europium by five bonds. However, the shift in a 1:1 mole ratio of $\text{Eu}(\text{DPM})_3$ and 3 was 900 Hz downfield for the 8-, 10-cis protons and 391 Hz downfield for the

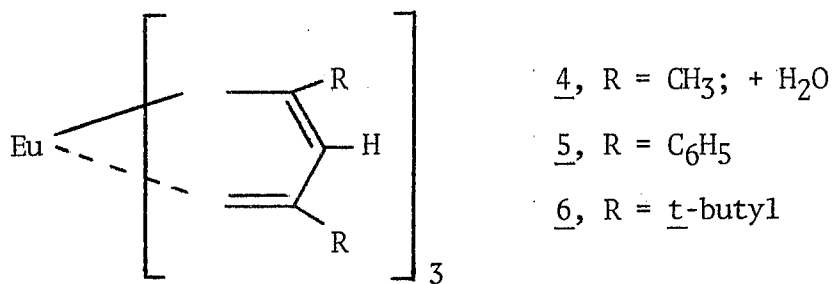
4-, 9-cis protons, the distance being 1.53 and 5.14 Å, respectively.

Shift reagents have often been used as a method for the determination of conformations of cyclic compounds. However, Williams and coworkers¹⁰ warn that when using these reagents to determine conformations in acyclic systems, it is not possible to fix the lanthanide to any rigid part of the molecule. Hence, the 'conformations' calculated are the weighted average geometries of the substrate interacting with the shift reagent. Further, they do not necessarily represent the weighted average conformation of the free substrate. This is especially true since the interaction of the substrate with the shift reagent can distort the geometry of the substrate and/or the position of the equilibrium between two conformations of nearly equal energy.

In bifunctional compounds coordination occurs chiefly at the stronger coordination atom at low concentrations of the shift reagent. At higher concentrations of the shift reagent coordination may occur also with the weaker group. This is applicable only for molecules in which the functional groups are rigidly separated by several carbon atoms.

Tris(dipivalomethanato)europium III is not the only compound that produces these shifts. Attempts have been made to use transition metal ions and complexes to induce similar chemical shifts. However, this generally results in broadening of the spectral lines. Two other tris-beta-diketonates of europium have been prepared for use as shift reagents. The hydrated acetylacetonate (4, $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$) produces very small chemical shifts because water decreases shifting ability. The dibenzoylmethanate (5, $\text{Eu}(\text{DBM})_3$) has also been prepared, but this compound

is insoluble in non-polar solvents. By far the most useful europium complex has been the dipivalomethanate (6, $\text{Eu}(\text{DPM})_3$). With this compound there is minimal broadening of the signal, it is sufficiently soluble in non-polar solvents, and there is the absence of interfering absorptions in the usual range of substrate spectra.



Another useful lanthanide examined has been praseodymium.¹¹ The dipivalomethanate of praseodymium ($\text{Pr}(\text{DPM})_3$) produces shifts to higher field. Line broadening produced by $\text{Pr}(\text{DPM})_3$ is slightly larger than that produced with $\text{Eu}(\text{DPM})_3$ and is greatest for those protons closest to the coordination site. The remaining lanthanides produce such signal broadening that much of the information about coupling constants is lost.

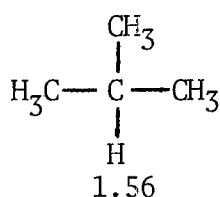
The purpose of this research was to look at the nmr spectra of several cubane derivatives to determine the effects of solvent, substituents and shift reagents on the chemical shift and line shape.

After the completion of this work, Farrell and co-workers¹² published the results of a similar study using a 100 MHz spectrometer. Their data is in close agreement with ours.

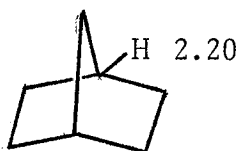
RESULTS AND DISCUSSION

Effect of Solvents

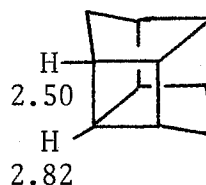
The hydrogens on cubane have an nmr chemical shift of 4.0 ppm.¹³ This represents a downfield shift from the normal tetrahedral carbon-hydrogen chemical shift. The hybridization of the carbon to which the proton is attached effects the diamagnetic shielding of the proton. In this case, the p character of the carbon orbitals involved in the skeletal C-C-C bonds and the s character of the exocyclic orbitals of the C-H bonds are increased due to ring strain. As the s character of the carbon atom of the C-H bond increases, the shielding of the proton is decreased and the signal is shifted downfield. The position of the cubane signal is related to the rehybridization of the C-H bonds in the molecule. The compounds below (7-11) show the effect of increased strain on the chemical shift on the methine protons.



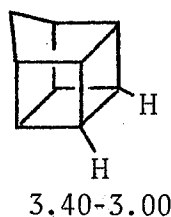
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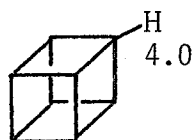
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10



11

The differences in chemical shift of bishomocubane,¹⁴ 9; homocubane,¹⁵ 10, and cubane,¹³ 11, are clearly related to differences in ring strain afforded by insertion of the methylene bridges in cubane and homocubane.

All of the cubane protons are equivalent because of the symmetry of the molecule and the nmr signal is a sharp singlet. However, the spectra of 10 and 11 contain broad signals for the methine protons. Homocubane has a broad unsymmetrical doublet at 3.40-3.00, no doubt due to the reduced symmetry in homocubane compared to cubane.

Bishomocubane has two types of methine protons: those adjacent to the methylene groups (2.50 δ) and the more strained ones at 2.82 δ . The lines in bishomocubane are not as broad as those in homocubane. However, the methylene protons in both 10 and 11 are singlets. McBee and co-workers¹⁵ suggest that the lack of coupling with the adjacent hydrogens may be attributable to the dihedral angle.

The shape of the signals in substituted cubanes parallels that in benzene more than adamantane and other caged compounds. The chemical shift of benzene protons is sensitive to the presence of electron-donating and electron-withdrawing substituents: electron-withdrawing substituents induce a downfield shift whereas electron-donating cause a shift to higher field.¹³ In the cubane system, weak electron-withdrawing substituents (e.g., -CH₂-OH) induce no splitting of the cubane resonances (cf. benzyl alcohol) while cubane derivatives with stronger electron-withdrawing substituents show a very complicated pattern (cf. benzoic acid). These effects are summarized in Table 2.

Table 2. The Effect of Substitution on the Chemical Shift of Benzene, Homocubane and Cubane.

Benzene¹⁴ (7.27)

<u>Substituent</u>	<u>Ortho</u>	<u>Meta</u>	<u>Para</u>	<u>Shape of Signal</u>
-COOH	7.90	7.37	7.44	multiplet
-NH ₂ ⁺	7.61	7.47	7.47	multiplet
-CH ₂ OH	7.15	7.15	7.15	singlet

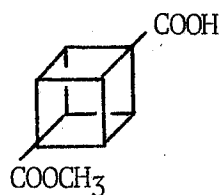
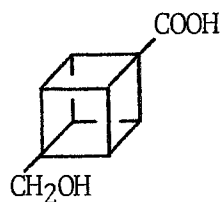
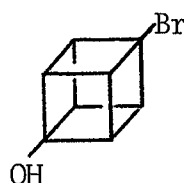
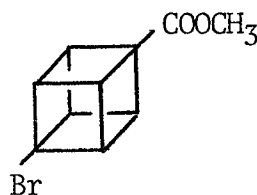
Homocubane¹⁵ (3.40-3.00 and -CH₂ 1.69)

<u>Substituent</u>	<u>Protons Adjacent to Substituent</u>	<u>-CH₂</u>	<u>-COOH Protons</u>	<u>Shape of Signal</u>
-COOH	3.72-3.05	1.72	11.45	multiplet
-NH ₂ ·HCl	3.68-3.17	1.73	-	multiplet
-CH ₂ NH ₂ ·HCl	3.42	1.67	-	unsym. doublet

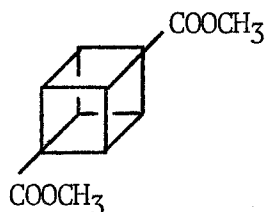
Cubane¹³ (4.00)

<u>Substituent</u>	<u>Cubane Protons</u>	<u>-COOH Protons</u>	<u>Shape of Signal</u>
-COOH	4.4-3.8	12.2	multiplet
-CH ₂ -OH	3.85	-	broad line, no large splitting

When both substituents are the same as in the 1,4-disubstituted cubanes, the signal for the cubane protons is a singlet. However, when the substituents are different, the equivalence of the cubane protons is removed and the shape of the signal varies significantly. For example, the signal of the half acid ester, 12, is a singlet for the cubane protons, while the signal for the acid alcohol, 13, is a multiplet. Klunder and Zwanengurg¹⁶ have explained the singlet in the *p*-hydroxybromocubane, 14, as not being unexpected because the shielding constants of a hydroxyl group and a bromine atom are almost the same. While this effect may explain the shape of the signal in some cases, it nevertheless does not explain the singlet for the cubane protons in *p*-bromocarbomethoxycubane, 15. With relatively large differences in shielding constants, the position of the cubane signal as well as the shape appears to be due to inductive and field effects.¹⁷

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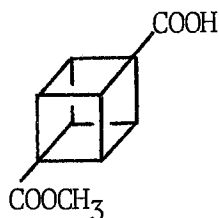
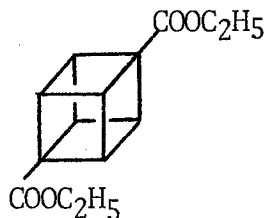
p-Dicarbomethoxycubane (16).--The spectrum of the diester consisted of two sharp singlets. The higher field signal was due to the methyl protons while the lower field signal is from the cubane protons. In dimethyl sulfoxide (DMSO- d_6), the signals were broadened slightly. The lines in the spectrum are usually broader in DMSO- d_6 because it is more viscous than most nmr solvents. There appears to be a significant solvent shift for both sets of protons. In benzene, the peak due to the methyl hydrogens is at 3.33 compared to 3.6 in carbon tetrachloride. In addition, the cubane hydrogens in benzene are at 3.90 and 4.15 in carbon tetrachloride. Below are the solvent shifts on this compound.

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<u>Solvent</u>	<u>δ(cubane)</u>	<u>δ(-CH₃)</u>	<u>δ(internal)</u>
CCl ₄	4.15	3.60	0.55
CDCl ₃	4.18	3.65	0.53
DMSO- d_6	4.12	3.58	0.54
CD ₃ CN	4.11	3.60	0.51
Benzene- d_6	3.90	3.33	0.51
Pyridine- d_5	4.04	3.57	0.46
Acetone- d_6	4.12	3.60	0.52
CD ₃ OD	4.13	3.65	0.48

Carbomethoxycubane Carboxylic Acid (12).--There are no significant solvent effects nor are there any significant changes in internal shifts for this compound, as illustrated below.

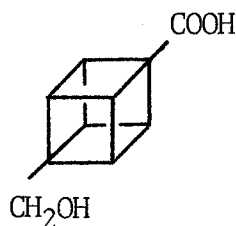
<u>Solvent</u>	<u>δ(cubane)</u>	<u>δ(-CH₃)</u>	<u>δ(internal)</u>
CCl ₄	(insoluble)		
CDCl ₃	4.21	3.67	0.54
DMSO-d ₆	4.09	3.58	0.51
CD ₃ CN	4.12	3.60	0.52
Benzene-d ₆	(insoluble)		
Pyridine-d ₅	4.13	3.60	0.53
Acetone-d ₆	4.13	3.61	0.52
CD ₃ OD	4.13	3.64	0.49

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p-Dicarboethoxycubane (17).--The spectra of this compound contain a singlet due to the cubane protons, a quartet for the methylene protons and a triplet for the methyl protons, as illustrated below.

<u>Solvent</u>	<u>δ (cubane)</u>	<u>δ (-CH₂)</u>	<u>δ (internal)</u>	<u>δ (-CH₃)</u>
CCl ₄	4.12	4.04	0.08	1.23
CDCl ₃	4.15	4.11	0.04	1.25
DMSO-d ₆	4.11	4.04	0.07	1.18
CD ₃ CN	4.09	4.05	0.04	1.19
Benzene-d ₆	3.94	3.91	0.02	0.96
Pyridine-d ₅	4.07	4.07	0.00	1.10
Acetone-d ₆	4.10	4.06	0.04	1.20
CD ₃ OD	4.12	4.09	0.02	1.22

p-Carboxycubylcarbinol (13).--While solvent shifts for this compound are relatively small, there is a significant internal shift with pyridine. Internal shifts are an indication of a specific interaction between the solvent and part of the molecule. This type of interaction has been reported in pyridine. Danyluk¹⁸ has suggested that the alignment of some groups along the polar pyridine ring is such that these groups lie off the plane of the ring. Therefore they will not be influenced significantly by the ring current of pyridine.



<u>Solvent</u>	<u>δ(cubane)</u>	<u>δ(-OH)</u>	<u>δ(-CH₂)</u>	<u>Internal δ(-OH)</u>	<u>Internal δ(-CH₂)</u>
CCl ₄	(insoluble)				
CDCl ₃	(insoluble)				
DMSO-d ₆	4.092-3.650	3.60	3.47	0.27	0.40
CDCl ₃	(insoluble)				
Benzene-d ₆	(insoluble)				
Pyridine-d ₅	4.267-3.650	under cubane signal	3.61	0.00	0.19
Acetone-d ₆	(insoluble)				
CD ₃ OD	4.175-3.725	3.69	3.61	0.26	0.34
<u>Shape of Signal</u>	symmetrical multiplet	broad singlet	broad singlet		

p-Bromocarbomethoxycubane (12).---The spectra of this compound contains two singlets. Solvent shifts are small; however, significant internal shifts are seen in pyridine.

<u>Solvent</u>	<u>δ(cubane)</u>	<u>δ(-CH₃)</u>	<u>δ(internal)</u>
CCl ₄	(insoluble)		
CDCl ₃	4.22	3.65	0.57
DMSO-d ₆	4.23	3.58	0.65
CD ₃ CN	(insoluble)		
Pyridine-d ₅	4.06	3.57	0.50
Benzene-d ₆	(insoluble)		
CD ₃ OD	(insoluble)		

The chemical shift data is summarized in Table 3.

Table 3. The Effect of Substituent and Solvent on the Proton Chemical Shift of Several 1,4-Disubstituted Cubanes Relative to the Chemical Shift of Cubane.*,**

Solvent	-COOCH ₃ , -COOCH ₃	-COOC ₂ H ₅ , -COOC ₂ H ₅	-COOCH ₃ , -Br	-COOCH ₃ , -COOH	-COOH, -CH ₂ OH
CCl ₄	0.15	0.12	insol.	insol.	insol.
CDCl ₃	0.18 (0.184)	0.15	0.22 (0.268)	0.21 (0.216)	insol.
DMSO-d ₆	0.12	0.11	0.23	0.09	0.09 to -0.35
CD ₃ CN	0.11	0.09	insol.	0.12	insol.
CD ₃ OD	0.13	0.12	insol.	0.13	0.18 to -0.28
C ₆ D ₆	-0.10 (-0.106)	-0.06	insol. (-0.139 to -0.205)	insol. (-0.074 to -0.149)	insol.
C ₅ D ₅ N	0.04 (0.053)	0.07	0.06 (0.105 to 0.029)	0.13 (0.163 to 0.077)	0.27 to -0.35
CD ₃ COCD ₃	0.12	0.10	insol.	0.13	insol.

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* The chemical shift for cubane is 4.0δ. Downfield shifts from cubane are indicated by positive numbers whereas upfield shifts are indicated by negative numbers.

** The shifts in parentheses are the chemical shift difference reported by Farrell et al. at 100 MHz (J. T. Edward, P. G. Farrell, and G. E. Langford, J. Amer. Chem. Soc., 98, 3075, 3085 (1976)).

the coordinating group while two protons are three bonds away. One explanation is that the position of the shift reagent relative to the cubane protons is such that the shift reagent is felt the same by all the cubane protons. Another explanation may lie in the close proximity of the ester groups. The cubane protons may be in the same effective environment because of rapid equilibrium between the shift reagent and the carbomethoxy groups.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A spectrometer at the operating temperature of 38°. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal tetramethylsilane as reference and were reproducible to ± 0.02 ppm. The shift reagent studies were all done using carbon tetrachloride as solvent. Deuterated solvents (chloroform-d, dimethylsulfoxide-d₆, acetonitrile-d₃, benzene-d₆, pyridine-d₅, and methyl alcohol-d₄) were purchased from Aldrich Chemical Company. The cubane derivatives used in this study were provided by Ms. Lily Lim.

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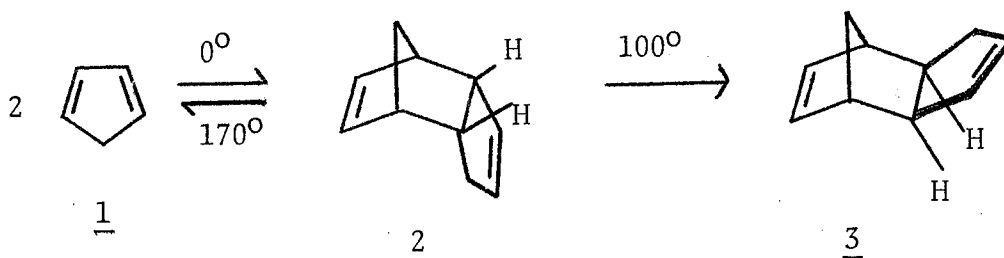
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PART II

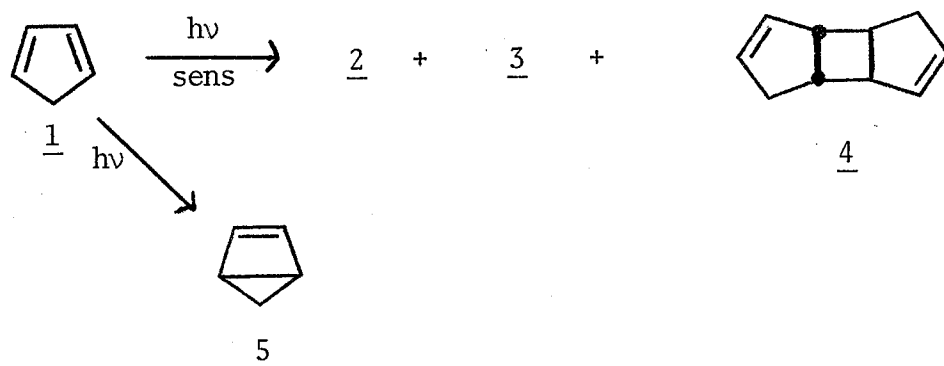
On the Mechanism of Photodimerization of Cyclopentadiene

INTRODUCTION

The thermal reactions of cyclopentadiene (1) have been studied thoroughly and are well understood.¹⁻³ Cyclopentadiene dimerizes at 0°, in typical Diels-Alder fashion, to produce exclusively endo-dicyclopentadiene (2). Formation of the endo-dimer over the thermodynamically more stable exo-dimer is accounted for by secondary orbital interactions.⁴ At 100° endo-dicyclopentadiene rearranges to the exo-isomer (3) and reverts to the monomer at 170°.

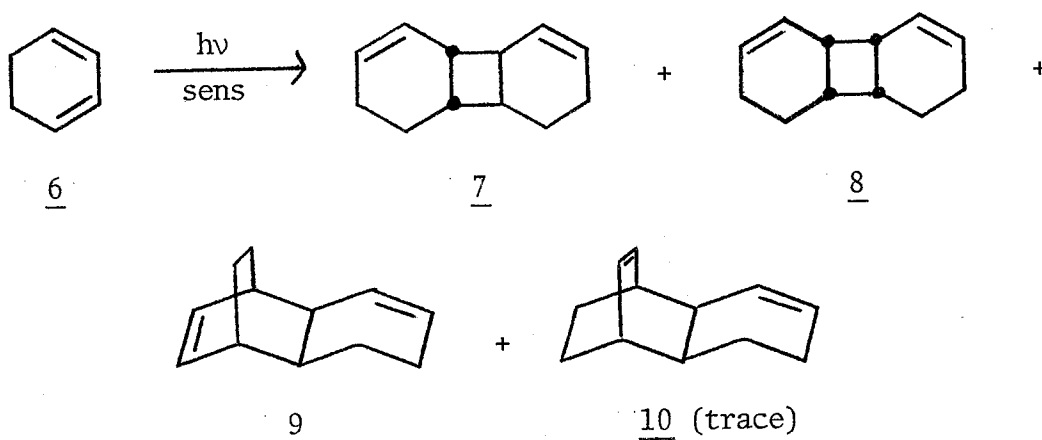


The photochemical behavior of cyclopentadiene depends on the reaction conditions. The unsensitized irradiation at low temperature gives bicyclo[2.1.0]pent-2-ene (5).⁵ When irradiated in the presence of benzophenone, a triplet sensitizer, cyclopentadiene gives rise to three dimers: endo-dicyclopentadiene (2), exo-dicyclopentadiene (3), and cis,trans,cis-tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (4)⁶ in a 1:1:1 ratio (after correction for thermal dimerization).

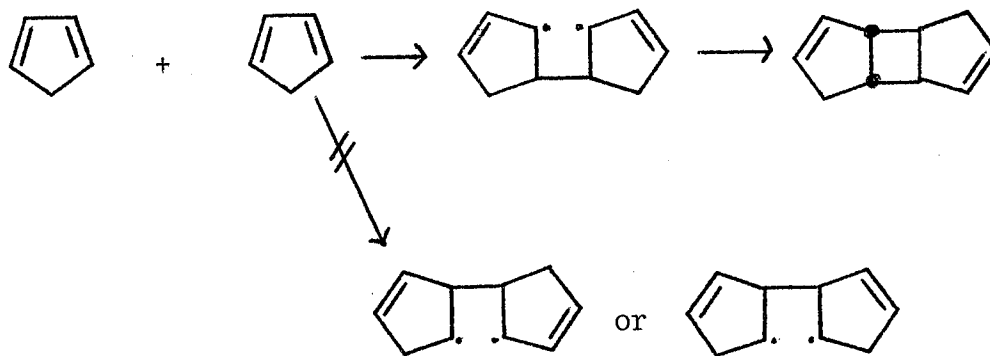


No explanation has yet been advanced for the formation of the three dimeric products 2-4 in equimolar amounts. Although the expected product should contain the tricyclo[5.3.0.0^{2,6}] ring skeleton arising from a ($\pi 2_s + \pi 2_s$) cycloaddition reaction, the stereochemistry should be cis,cis,cis- rather than cis,trans,cis-.² Thus, none of the products are consistent with orbital symmetry predictions. There are at least two explanations for this apparent violation. First, all three dimers are formed from the same excited state. Of the various primary photochemical processes⁷ available to cyclopentadiene, the excited state responsible for product formation in the photochemical reaction is very similar (structurally and energetically) to the state responsible for dimer formation in the thermal reaction. The second interpretation is that since benzophenone is a known triplet sensitizer, the reaction proceeds at some point through the triplet excited state of cyclopentadiene. Dimerization via the triplet excited state may not be concerted. Since Woodward-Hoffman rules apply only to concerted reactions, this violation can be accommodated by a stepwise process.

Photosensitized dimerization of 1,3-cyclohexadiene (6) gives trans,cis,trans-tricyclo[6.4.0.0^{2,7}]-dodeca-3,11-diene (7), the corresponding cis,cis,cis- isomer, 8, and exo-dicyclopentadiene (9) in a 3:1:1 ratio. Traces of endo-dicyclohexadiene (10) are also formed.



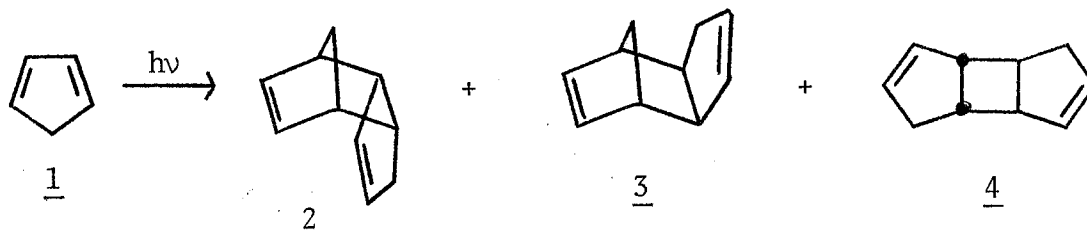
Thermal dimerization of cyclohexadiene gives only the expected Diels-Alder dimers, 9 and 10, in a 1:4 ratio.⁸ The dimers 7 and 8 contain the expected ring skeletons for the photochemical reaction according to the orbital rules, but this reaction also does not follow the predictions exactly. In both cases, the products seem to arise via the more stable diradical as follows:⁶



The research described in this part of the thesis was an attempt to reinvestigate the sensitized photochemistry of cyclopentadiene in order to offer a rational account for the product distribution and to test the applicability of orbital symmetry rules to the photochemistry of this system.

RESULTS AND DISCUSSION

The irradiation of cyclopentadiene in the presence of benzophenone is a classic example of a sensitized photochemical reaction.



Thermal dimerization occurs as low as 0° . If the irradiations were done at a significantly lower temperature (-60°), this should preclude thermal dimerization or at least slow down the thermal reaction to the point that the photochemical reaction is favored. Hence, the initial phase of this research was planned to investigate this reaction at -60° .

The irradiations reported on this system were attempted using a high pressure ultraviolet lamp. No results using a low pressure ultraviolet lamp had been reported for the cyclopentadiene photochemical reaction. The low pressure lamp has the advantage of providing more intense light at shorter wavelengths than is available with medium and high pressure lamps. Since cyclopentadiene has a λ_{max} at 239 nm, it appeared that an ultraviolet light source stronger at shorter wavelengths would give additional information about the system. To provide for more intense light if reaction did not occur, plans were made to irradiate cyclopentadiene using a high pressure lamp. The high pressure lamp, in addition to being a much more intense light source, has a

broader bandwidth. The irradiations were planned two ways: unsensitized and sensitized with benzophenone, through a quartz immersion well.

Cyclopentadiene was irradiated through quartz at -60° using a Nester and Faust low pressure ultraviolet lamp with maximum output at 254 nm. The progress of the reaction was monitored by nuclear magnetic resonance spectroscopy. Aliquots removed from the reaction after the irradiation had gone for 300 minutes showed no change.

Cyclopentadiene was then irradiated in the presence of benzophenone, a triplet sensitizer, at -60° . The nmr spectrum of a sample from the irradiating flask after 14 hours of irradiation showed no change in the cyclopentadiene. The sensitized irradiation of cyclopentadiene was continued at 0° . After five hours of irradiation, the color of the solution was yellow. The nmr spectrum of the product indicated only thermal dimerization had occurred.

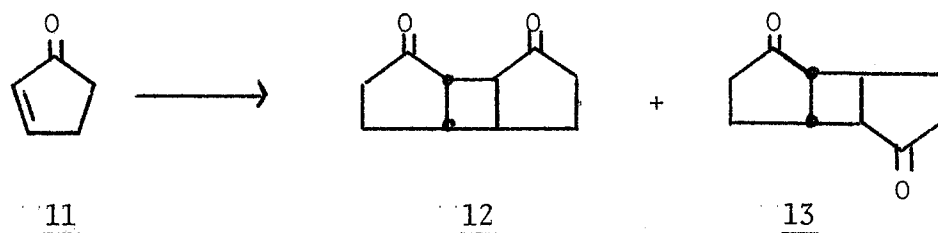
The unsensitized irradiation of cyclopentadiene was carried out at $4-8^{\circ}$. Nuclear magnetic resonance spectra of aliquots, recorded from 0 to 38 hours of irradiation, indicated that the thermal reaction was taking place, but showed no apparent evidence of a photochemical reaction.

Irradiation of cyclopentadiene using a Hanovia 450 watt high pressure ultraviolet lamp was carried out at -60° . Samples taken for nmr spectra after six hours showed no reaction taking place. In addition, a dark coating formed on the immersion well which interfered with the light passing through the quartz. The irradiation was continued with a Vycor filter for an additional five hours. An nmr spectrum of the irradiated

solution showed no changes in the compound. Benzophenone was added to the above solution and the solution was irradiated for three hours. Still no changes were observed in the nmr spectrum.

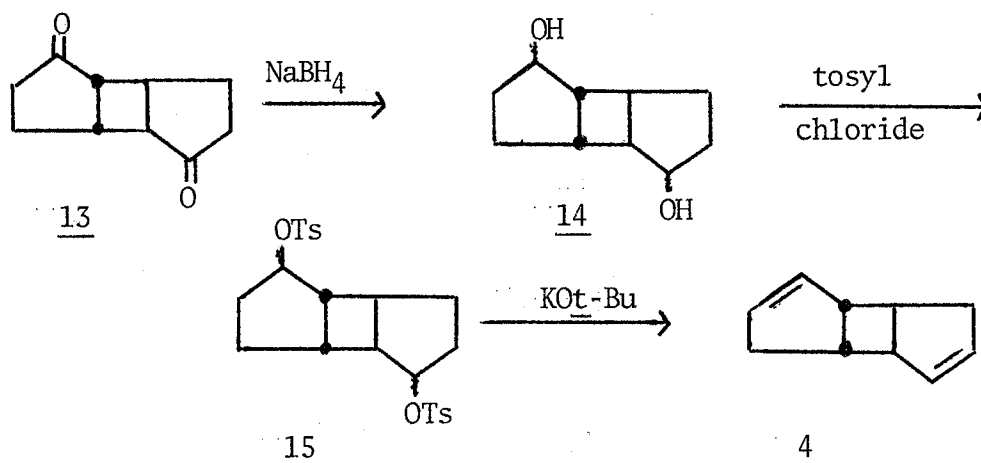
One consequence of the Woodward-Hoffman rules is that if any concerted reaction proceeds thermally it is not allowed photochemically, and vice versa. It also follows that if a reaction proceeds via a photochemical or a thermal path, then its reverse reaction should follow the same path. Since the approach from the cyclopentadiene side of this reaction was not promising, attention was directed toward the reverse reaction, i.e., the irradiation of tricyclo[5.3.0.0^{2,6}]3,8-decadiene, one of the products from the sensitized irradiation of cyclopentadiene.

One method for the preparation of tricyclo[5.3.0.0^{2,6}]3,8-decadiene is from tricyclo[5.3.0.0^{2,6}]3,8-decadione. The most straight-forward synthesis of tricyclo[5.3.0.0^{2,6}]3,8-decadione is the one suggested by Eaton.⁹



Cyclopentenone (11) was irradiated for 24 hours through Pyrex. This gave both tricyclo[5.3.0.0^{2,6}]3,8-decadione (12), the head-to-head dione, and tricyclo[5.3.0.0^{2,6}]3,9-decadione (13), the head-to-tail dione. The two were separated with carbon tetrachloride, the head-to-tail dione being less soluble. The procedure of Hammond and co-workers¹⁰ was used

for the remainder of the synthesis of tricyclo[5.3.0.^{02,6}]3,8-decadiene, the head-to-tail diene, as follows:



The head-to-tail dione 13 was reduced with sodium borohydride in sodium hydroxide to give the head-to-tail diol 14. This product was reacted with tosyl chloride in pyridine for five hours to form the corresponding tosylate 15. Tricyclo[5.3.0.^{02,6}]3,8-decadiene (4) was prepared from the tosylate by refluxing with potassium *t*-butoxide in *t*-butyl alcohol for 24 hours.

Initially, the diene prepared above was irradiated four hours in acetone- d_6 . The nmr spectrum of the solution did not resemble spectra of cyclopentadiene nor did it resemble spectra of *endo*-dicyclopentadiene. In addition, the spectrum indicated a possible reaction with the acetone and possible formation of the oxetane with a complex multiplet at δ 3.3-3.9 ppm.

Since the diene decomposed after four hours of irradiation, a shorter irradiation time was indicated. The diene was dissolved in acetone and the irradiation carefully monitored by nmr. Spectra taken at various intervals still indicated a reaction was taking place between acetone

and the diene. This reaction interfered with or may have even prevented the desired photochemical reaction from occurring.

Overall, this series of experiments indicate that the photochemistry of cyclopentadiene is difficult to study because of its rapid thermal dimerization. At very low temperatures (-60°) it was not possible to obtain any reaction, photochemical or thermal, using either low or high pressure ultraviolet lamps. At $0-8^{\circ}$, the thermal reaction does occur and prevents a thorough study of the photochemistry. The thermal reaction is at best only slowed down by lowering the temperatures. An attempt to study the reaction by synthesizing one of the products, tricyclo[5.3.0.0^{2,6}]3,8-decadiene and looking at the reversible reaction to cyclopentadiene was also unsuccessful. At the conditions studied, irradiation of the head-to-tail diene resulted in decomposition and/or interfering side reactions that prevented the desired photochemical reaction from occurring.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A spectrometer using internal tetramethylsilane (TMS) as a reference. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal TMS. Carbon tetrachloride or deuterated solvents were used to make spectral solutions. A Beckman IR-5A infrared spectrophotometer was used to record infrared spectra. Spectra were calibrated against the 6.25μ band of polystyrene film. Ultraviolet light sources were a Nester and Faust low pressure ultraviolet lamp emitting strongest light at 254nm and a Hanovia 450-watt high pressure lamp. Samples were irradiated in either a quartz immersion well which transmitted light above 190nm or a Pyrex irradiating chamber which transmitted light above 300nm. Low pressure irradiations were done only through quartz because of its transmittance properties. On the other hand, high pressure irradiations were done through quartz and Pyrex.

1,3-Cyclopentadiene.--Cyclopentadiene was prepared from commercially obtained dicyclopentadiene (Eastman Organics) by the distillation described by Moffett.¹¹ The cyclopentadiene was collected and stored under Dry Ice; nmr (CCl_4) δ 2.30 (m, 2), 5.98 (sym m, 4) ppm.

Photodimerization of 2-Cyclopentenone.--2-Cyclopentenone was irradiated according to the procedure of Eaton⁹ to cis,trans,cis-tricyclo[5.3.0.0^{2,6}]3,8-decadione (33.9 g, 41%).

trans-Ditosyloxytricyclo[5.3.0.0^{2,6}]3,8-decane.--Tricyclo[5.3.0.0^{2,6}]3,8-decadione was reduced with sodium borohydride by the method of Hammond and co-workers⁸ (7.4-8.2 g, 74-82%) to form the corresponding diol. The

tosylate was then prepared from the diol and tosyl chloride; mp 162-164^o dec (lit.⁸ mp 158-159^o dec), 3.6-5.3 g, 63-93%.

trans-Tricyclo[5.3.0.0^{2,6}]3,8-decadiene.--The compound was prepared by the method of Hammond and co-workers.¹⁰ trans-Ditosyloxytricyclo[5.3.0.0^{2,6}]3,8-decane (9.55 g, 0.02 m) was dissolved in 550 ml of t-butyl alcohol. The mixture was stirred magnetically. Potassium t-butoxide (15.6 g, 0.13 m) was added to the stirring solution. The reaction flask was fitted with a reflux condenser protected with a drying tube. The mixture refluxed for 24 hr and was cooled in an ice bath. Cold water (500 ml) was added to the reaction mixture and the mixture filtered by suction filtration. The resulting aqueous phase was extracted 4 times with 200-ml portions of pentane. The pentane extracts were combined and washed twice with 50-ml portions of water and with brine. The pentane layer was then dried over sodium sulfate. After standing a few hours, the pentane solution was filtered by gravity filtration and the pentane removed on a rotary evaporator. The yield of crude diene was 3.44 g. The crude product was distilled under vacuum at 0.1 mm pressure. The product distilled at 80^o, yield 0.53 g.

Irradiation of trans-Tricyclo[5.3.0.0^{2,6}]3,8-decadiene.--trans-Tricyclo[5.3.0.0^{2,6}]3,8-decadiene (0.14 g, 0.0011 m) was dissolved in acetone-d₆, a triplet sensitizer. The solution was placed in a water-cooled Pyrex chamber and irradiated with a Hanovia 450-watt mercury arc lamp. Aliquots of the diene were removed after 4 and 5 hr of irradiation. Nuclear magnetic resonance spectra were taken of these aliquots and indicated probable decomposition of the diene.

A larger sample of the diene (0.39 g, 0.003 m), dissolved in acetone, was irradiated in the apparatus described above. Aliquots were taken after the solution had been irradiated 0.25, 0.75, 1.25, 1.75, 2.75, 3.50 and 4.50 hr for mmr spectra.

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